DIFFRACTION PATTERN OF SULPHURIC ACID AT DIFFERENT CONCENTRATIONS

By H. N. BOSE

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Plate XI

ABSTRACT. In the present investigation, X-ray diffraction of pure acid and at concentrations corresponding to the formulae H_2SO_4, H_2O; H_2SO_4, $2H_2O$; H_2SO_4, $3H_2O$; H_2SO_4, $10H_2O$; H_2SO_4, $20H_2O$, etc., were studied. Pure sulphuric acid yields two well-defined bands (spacings 4.07 and 7.98 A.U.) with very little general scattering thereby following the general behaviour of highly associated liquids, though the inner band remained undetected so long. With dilution, the main band dilated and at the same time underwent an increase in diffuseness till at high dilution the familiar band of water made its appearance and the main peak of sulphuric acid nearly coincided with the first band of water (3.24 A.U.). Considering the main peak at largest angle at any dilution, the spacing of the acid was found to be intermediate between those of pure sulphuric acid (4.07 A.U.) and pure water (3.24 A.U.). The spacing underwent a violent change when the concentration was changed to H_2SO_4, H_2O and again at H_2SO_4, $20H_2O$.

At concentrations corresponding to H_2SO_4, $2H_2O$ and H_2SO_4, $3H_2O$ the spacings remained constant 3.54 A.U. This may be taken to indicate something akin to hydrate formation. Sulphuric acid, it is known, ionises in aqueous solution in two stages. But apart from making the bands a bit diffuse, this was found to have little effect on the X-ray diffraction pattern. This is but what can be expected for (SO_4), (HSO_3) and (H_2SO_4) have almost the same dimension and scattering due to H^+ is negligible. The general behaviour of sulphuric acid has been tried to be explained qualitatively by extending the ideas of Lenard Jones.

INTRODUCTION

The affinity of sulphuric acid for water naturally suggests the possible formation of definite compounds or hydrates and the existence of such hydrates has been demonstrated in various ways. The freezing point curve for mixtures of two substances is usually regarded as affording a definite evidence of the occurrence or otherwise of chemical combination between the constituents and with mixtures of sulphuric acid and water definite results are obtained. With sulphur trioxide and water as two components, maxima on the freezing curve occur at proportions corresponding to the composition of the following compounds[1]: SO_3 : H_2SO_4; H_2SO_4, H_2O; H_2SO_4, $2H_2O$; H_2SO_4, $4H_2O$. Thus the existence of a mono-, di- and a tetra hydrate of sulphuric acid in the solid condition is proved but the possibilities of other hydrates, for instance, H_2SO_4, $3H_2O$; H_2SO_4, $5H_2O$; and H_2SO_4, $12H_2O$ are not excluded.

Sulphuric monohydrate, $H_2SO_4\ H_2O$ crystallises from the acid of the corresponding concentration, in hexagonal prisms and melts at 9°C, the di-hydrate H_2SO_4, $2H_2O$ melts at -37°C and the tetra hydrate H_2SO_4, $4H_2O$ at $-24°.5$C. H Shiba and T. Walnabe[2] were the first to study the diffraction of X-rays by aqueous solution of sulphuric acid at four concentrations. They reported a contraction of the halo with increase in concentration. In their experiments, the central undeflected beam of X-rays was not cut off and consequently they were not able to record any change in the diffraction pattern with change in concentration at a very small angle of scattering.

R. S. Krishnan[3] investigated the diffraction of X-rays by aqueous solution of sulphuric acid and attempted to correlate his results with those obtained from Raman effect data.

X-ray diffraction of pure acid and at concentrations corresponding to formulae H_2SO_4, H_2O ; H_2SO_4, $2H_2O$: H_2SO_4, $3H_2O$; H_2SO_4, $10H_2O$; H_2SO_4 $20H_2O$ were undertaken to investigate if any information regarding such hydrate formation could be obtained purely from diffraction photograph We could detect in the present experiment, apart from the usual strong band, another inner weak band, which was not observed by any of the previous investigators.

EXPERIMENTAL TECHNIQUE

The arrangement of apparatus in the present investigation was the same as is generally used in powder photograph. The X-ray bulb was a demountable porcelain Hadding tube with a copper anticathode without any rectifying device. A hemicylindrical camera of radius 2.85 c.m. was used with a slit system having an aperture of .8 m.m. Liquid cells were prepared in a specially prepared thin walled glass capillary tube which was filled with a freshly prepared acid of required concentration, sealed at both ends so that the concentration remained unchanged and was then fixed to the cap of the slit with a bit of wax. The central beam was cut off with a lead cap placed on the film holder. The contribution of the container tube to the diffraction pattern was almost negligible as was observed in a trial experiment. The bore of the glass capillary was approximately kept constant (about 0.8 m.m.).

Sulphuric acid labelled ' Merck ' for analytical Reagent (99.2%) was used in this experiment. The different concentrations were prepared by adding 5 c.c. of the pure acid with the help of a graduated pipette to the calculated amount of water.

RESULTS (PURE SULPHURIC ACID)

The diffraction pattern of pure sulphuric acid consists of two sharp bands. The band at larger angles is much stronger than the other. Besides these, a central corona extending almost up to the inside of the inner band could be noticed. The diameters and the corresponding values of Bragg spacings are given in the Table for all the concentrations.

Fig. 1.

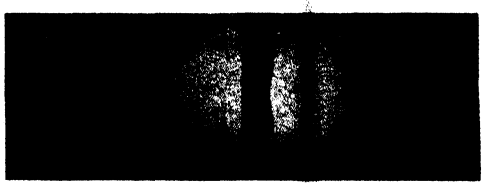

Fig. 2.

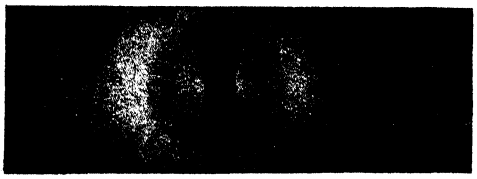

Fig. 3.

Fig. 1.—$H_2SO_4 + H_2O$

Fig. 2.—Pure H_2SO_4

Fig. 3.—$H_2SO_4 + 20H_2O$

The aqueous solution of sulphuric acid of concentration corresponding to the formula H_2SO_4, H_2O (*i.e.*, sulphuric acid and water being present in the proportion of 98 gms. to 18 gms.) was next prepared and its diffraction pattern was investigated. The conspicuous change that differentiates it from the previous one, *i.e.*, for pure acid, lies not only in the increase of diameters of the bands but also they are more diffuse, or in other words, the Bragg-spacings corresponding to the maximum intensity of the bands have decreased and at the same time they are more diffuse thus increasing the band width. The shift in the position of the maximum intensity of the band towards larger angle and the loss of sharpness are more pronounced in the case of the outer band.

TABLE

Aqueous Sulphuric Acid

Hemicylindrical Camera of radius 2.85 c.m.

Molecular proportion	Strength of sol. by weight	Approx. p. c. contraction of volume	No.	Angle of difiraction corresponding to maximum intensity	'd' (A.U.)
Pure H_2SO_4	99.2%		1	10°54′	4.07
			2	5°32′	7.98
H_2SO_4, H_2O	84.5%	8.6%	1	12°22′	3.6
			2	6°2′	7.32
H_2SO_4, $2H_2O$	73.1%	9.5%	1	12°34′	3.54
			2		
H_2SO_4, $3H_2O$	64.5%	9.2%	1	12°34′	3.54
			2	6°2′	7.32
H_2SO_4, $10H_2O$	35.2%	5.8%	1	12°48′	3.47
			2	7°2′	6.28
H_2SO_4, $20H_2O$	21.4%	4.4%	1	13°34′	3.28
			2	7°2′	6.28
			3	23°43′	1.91
			4	?	
H_2SO_4 Water	50%	6.4 %	1	12°43′	3.50

In the diffraction pattern at concentrations corresponding to H_2SO_4, $2H_2O$ and H_2SO_4, $3H_2O$, changes of similar nature are observed ; with concentration H_2SO_4, $10H_2O$, besides the changes stated, the pattern was remarkable by the appearance of a very weak band at still larger angles. For the concentration H_2SO_4, $20H_2O$

the third band appeared with great intensity and a fourth one could be suspected at a still larger angle. These additional bands were found to correspond to those of water.

R. S. Krishnan reported previously of the absence of any band at 50% concentration. In the present investigation, however, a diffuse band could be obtained even at this concentration.

The results are given in the table. In the first column, are given the molecular proportions of H_2SO_4 and H_2O, and in the second, the amount of H_2SO_4 present in 100 gms. of the solution. The third column contains percentage contraction corresponding to the concentration, the angle of maximum scattering and the corresponding Bragg spacing are listed in the fourth and fifth columns respectively.

All measurements, given here, were made with the help of a glass scale on the negative Generally, the bands are neither sharp nor intense, so that the order of accuracy, usually claimed in the measurement of sharp rings, is not attainable here. In the present case the first band is, in most of the concentrations, very weak and diffuse, hence the measurements on the first band are to be taken as approximate and the shift in the position of this band is likely to be less reliable.

DISCUSSION OF THE RESULTS

The presence of well-defined bands, with very little general scattering in the diffraction pattern of the pure acid is indicative of the existence of a very orderly arrangement of the molecules. Sulphuric acid is a highly associated liquid and associated liquids, in general, exhibit a secondary maximum in addition to the principal one We find that sulphuric acid is also not an exception and shows, as expected, two bands in the diffraction pattern.

P. Krishnamurti[4] has studied various liquid mixtures at different concentrations. For completely miscible liquids, he found that the diffraction pattern is different from that of either of the constituents. The main peak is invariably of intermediate spacing. With dilution, the main peak dilates and ultimately coincides with that of the major constituent. It is found that the liquids of this type are all associated. Similar results are also obtained for sulphuric acid. The main band of pure sulphuric acid and pure water have spacings 4.07 A.U. and 3.24 A.U. respectively, we find that spacings for other concentrations are intermediate between these two limits. In the first concentrations (H_2SO_4, H_2O) the spacing changes considerably (4.07 A.U. for pure H_2SO_4 to 3.6 A.U.). The change in spacing when the acid is diluted from H_2SO_4, $10H_2O$ to H_2SO_4, $20H_2O$, is also large. At concentrations H_2SO_4, $2H_2O$ and H_2SO_4, $3H_2O$ the spacings remain unaltered (3.54 A). These seem to indicate the presence of some hydrate of definite composition near about these concentrations. The presence of the inner

band in all the concentrations is rather puzzling. Similar inner ring whose spacings remain almost constant in all concentrations were also noticed by P. Krishnamurthy in certain liquids like glycerine, etc. It is peculiar that the spacing of this inner band is always almost double the spacing of the main band.

For solids, Lennard Jones[5] has shown that band spacing of an ionic crystal decreases with the decrease in particle size. A very quantitative explanation of the results may also be obtained by extending his ideas for this case. In the pure state, sulphuric acid consists of groups of molecules which are responsible for the pattern. We may assume that in the process of dilution the number of molecules constituting the groups decreases which results not only in a diminution of the size of the groups but also in the band spacing. The other effect of dilution, *i.e.*, the increase in the diffuseness of the bands, is perhaps due to the fact that as dilution proceeds, the molecules forming a particular group become less and less permanent. This proceeds till the water content of the solution is sufficient to produce a pattern. This explains in general the behaviour of the solution. Before this final stage is reached it is, however, possible that there may be certain intermediate concentrations when the groups will be consisting of molecules of both kinds. Another factor which influences the nature and size of halo is the change in volume on mixing. Mixture of sulphuric acid and water is accompanied by changes in volume. This factor influences the patterns since it affects the distance between neighbouring molecules but the computation of the nature of its dependence on the spacing is evidently very difficult and is not possible at this stage.

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KHAIRA LABORATORY OF PHYSICS,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA

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